



Chemical Analysis of Floor Sweepings From Aberdeen Proving Ground Building 1107

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Abstract

A sample of floor sweepings taken from Building 1107 of the Aberdeen Proving Ground (APG) was provided for analysis with the request that it be examined for the presence of energetic materials. An analysis was performed using desorption/pyrolysis-gas chromatography-mass spectroscopy (GC-MS) and differential scanning calorimetry (DSC). No evidence of the presence of energetic materials in the sample was found.

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1. Introduction

In November 1998, a sample of materials swept up from the floor of Building 1107 was provided by Mr. Tom Jones of the U.S. Army Research Laboratory (ARL) Risk Management Office for analysis with the specific request that the sample be examined for the presence of energetic materials. The sample was composed of sand, wood chips and splinters, plastic, paper, metal foil, and plant matter (grass and sticks). By far, the largest component was sand.

2. Sample Preparation

Since the requested analysis was simply to look for evidence of energetic material, but no *specific* energetic material, a very generic approach was taken to prepare the sample for analysis. An outline of this process is given in Figure 1. Samples referred to as A, B, and C throughout this report are also identified in that figure.

Since it is known that most energetic materials are soluble in acetone, this solvent was used to extract the whole of the floor-sweeping sample. Towards this end, 300 mL of acetone were added to the jar containing the sample. The mixture was stirred for several minutes and then allowed to sit overnight. Following this extraction period, the sample was filtered and the acetone solution collected. The filter paper was washed several times with clean acetone to ensure that no energetic material would remain on the paper. The filtrate was allowed to dry, analyzed, and found to contain a large fraction of hydrocarbons (oils and grease), which might obscure the presence of energetic materials. For this reason, the material was extracted with methylene chloride (a good solvent for hydrocarbons and some energetic materials), resulting in a clear, brown solution and a solid residue. The residue was then washed with acetone to recover any acetone soluble materials that may have been present.

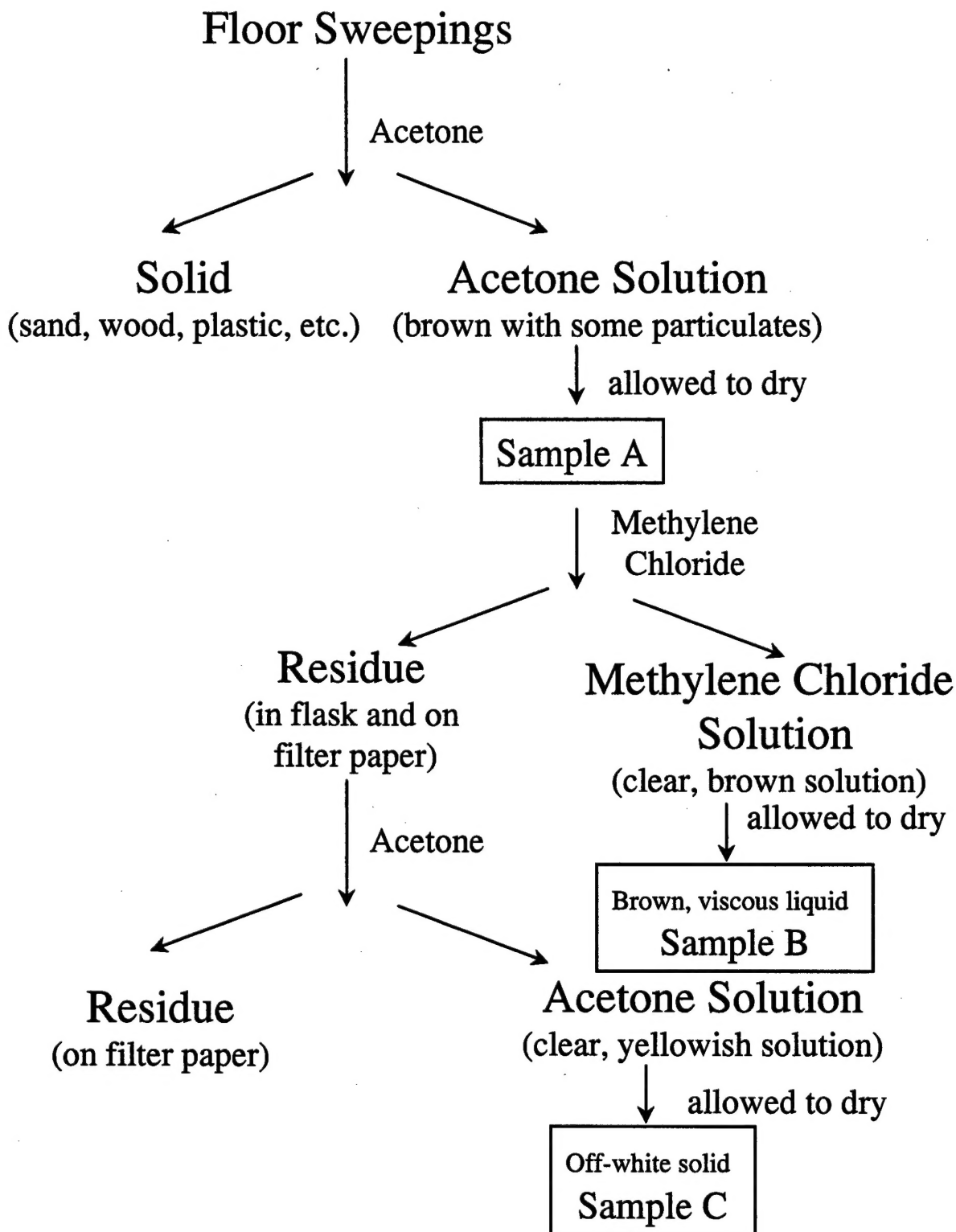


Figure 1. Sample Preparation Scheme.

3. Experimental

3.1 Desorption/Pyrolysis-Gas Chromatography-Mass Spectroscopy (GC-MS).

Milligram-sized samples were loaded into a small quartz tube containing a plug of glass wool (to hold the sample in place). The quartz tube was loaded into the coils of a CDS Pyroprobe 2000. The Pyroprobe was then inserted into a heated, valved interface chamber, which was, in turn, connected to the splitless injector of a Hewlett Packard gas chromatography-Fourier transform infrared-mass spectrometry (GC-FTIR-MS) system (Model 5890 GC, Model 5970 MSD, and Model 5965 IRD). The gas chromatography (GC) column used was a J&W Scientific capillary column (0.25 mm \times 15 m; 0.25- μ m DB5 film). The GC injector temperature was 200° C. The oven-temperature program used was as follows: 50° C isothermal for 1 min; 40° C/min to 250° C; and 250° C isothermal until run was manually terminated. The Pyroprobe interface was held at 175° C. A 20-s pulse was given via the Pyroprobe coil to achieve the desorption or pyrolysis of the residue.

3.2 Differential Scanning Calorimetry (DSC). Thermal analysis was performed with a Mettler-Toledo DSC30 fitted with a liquid-nitrogen-cooling accessory. Data were processed with Mettler Graphware software. Samples were heated under an argon atmosphere (flow rate: 10 mL/min) in pierced aluminum pans. The heating rate was 10° C/min, and the heating range was from 50 to 250° C.

4. Results

Since the analysis was not being performed for any particular energetic material, and since it would have been impractical to screen for all possible energetic materials in the presence of so many other materials that were extracted from the floor-sweeping sample, an unusual approach had to be taken. This was to pyrolyze the samples and look for the presence of nitrogen oxides. All of the energetic materials commonly used at Aberdeen Proving Ground (APG) that could possibly be in the floor-sweeping sample (e.g., NC, RDX, HMX, PETN, NG, DEGDN, NQ) will generate nitrogen oxides under the conditions of the previously described experiment. Nitrogen oxides may be

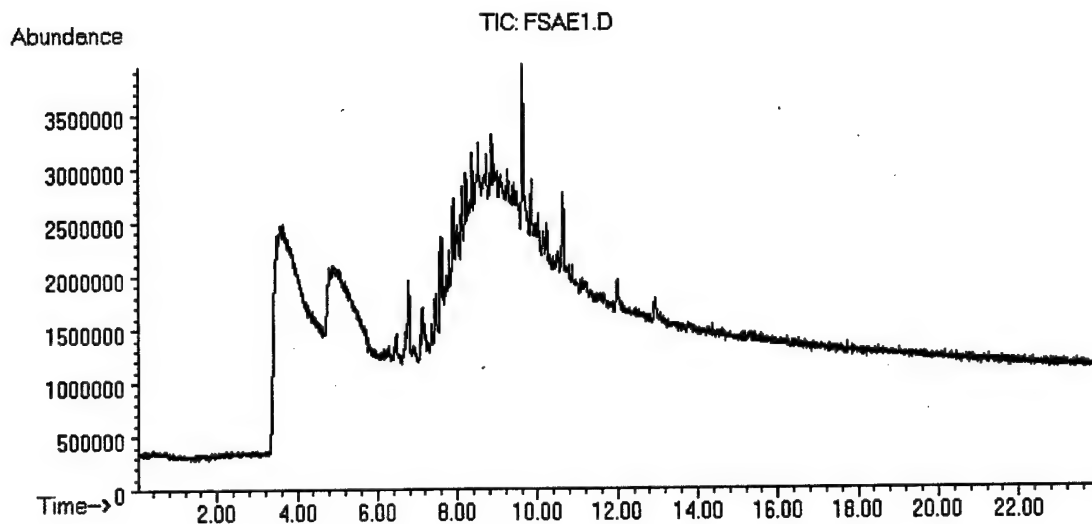
detected by MS and are evidenced by the masses 30 (NO), 44 (N₂O), and 46 (NO₂). The same masses may be generated by other materials. For example, mass 30 can be generated by formaldehyde (CH₂O) and mass 44 can be generated by carbon dioxide (CO₂). Table 1 gives some common pyrolysis/combustion products for energetic materials. Other features in a gas chromatogram and mass spectrum can often be used to distinguish between coincidental masses.

Table 1. Names and Masses of Some Common Gaseous Pyrolysis/Combustion Products

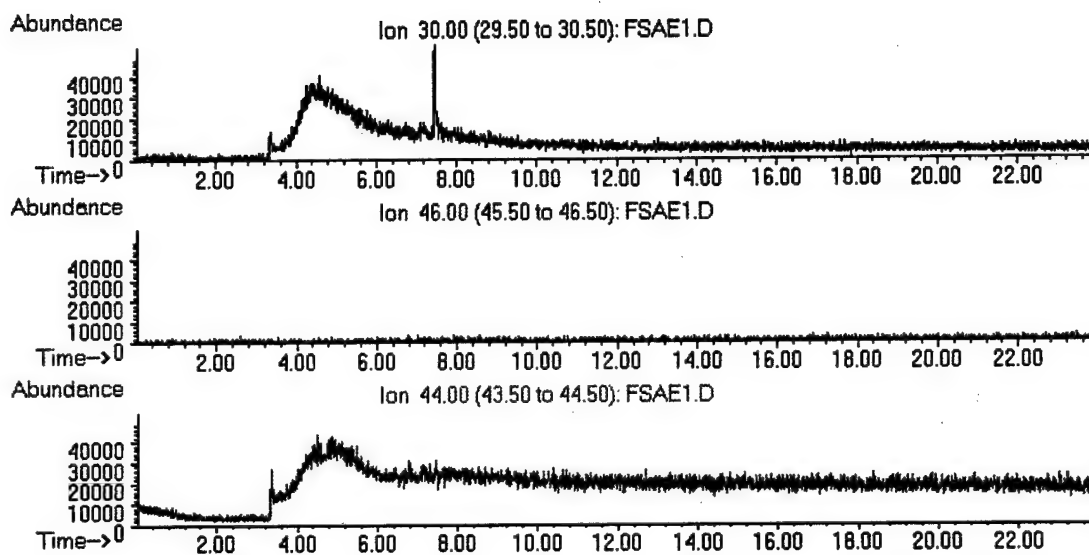
Gas	Mass
Water (H ₂ O)	18
Nitrogen (N ₂)	28
Carbon Monoxide (CO)	28
Nitric Oxide (NO)	30
Formaldehyde (CH ₂ O)	30
Carbon Dioxide (CO ₂)	44
Nitrous Oxide (N ₂ O)	44
Nitrogen Dioxide (NO ₂)	46

Analysis of the acetone extract of the original floor-sweeping sample (sample A) resulted in a very complex chromatogram (Figure 2). Most of the peaks in the chromatogram were identified by MS to be hydrocarbons. Extracted ion chromatograms of the masses 30, 44, and 46 (Figure 2 [b]) indicated the presence of masses 30 and 44, but not 46, when the sample was pyrolyzed at 175° C. These results indicated that it was possible that energetic materials may have been present in the sample and that further analysis was required.

To try to separate some of the components in the floor-sweeping extract, a second extraction was performed, as indicated in the scheme in Figure 1. The result of this extraction was a relatively large amount of a brown, viscous liquid (sample B) and a very small amount of an off-white solid. The total ion chromatogram and selected ion chromatograms for sample B are given in Figure 3. There

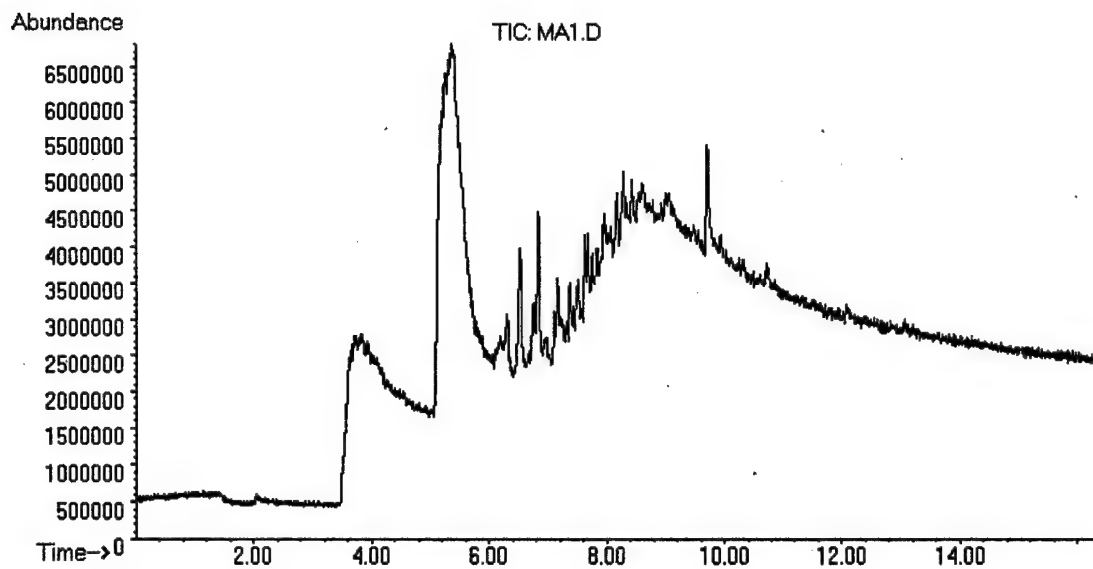


(a)

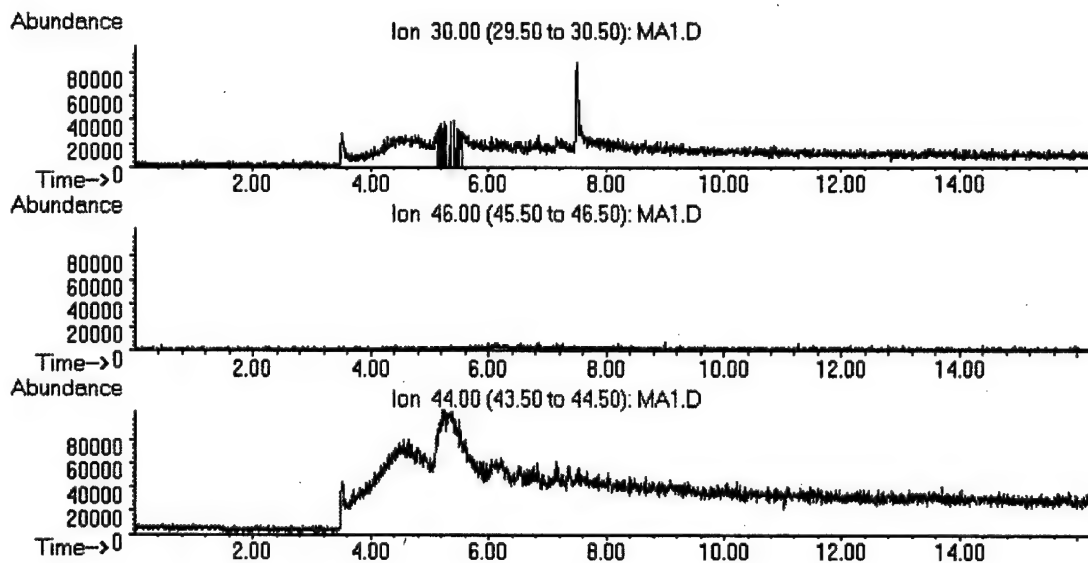


(b)

**Figure 2. Gas Chromatograms for Sample A, Pulse Temperature = 175° C:
 (a) Total Ion Chromatogram and (b) Selected Ion Chromatograms.**



(a)



(b)

Figure 3. Gas Chromatograms for Sample B, Pulse Temperature = 175° C:
(a) Total Ion Chromatogram and (b) Selected Ion Chromatograms.

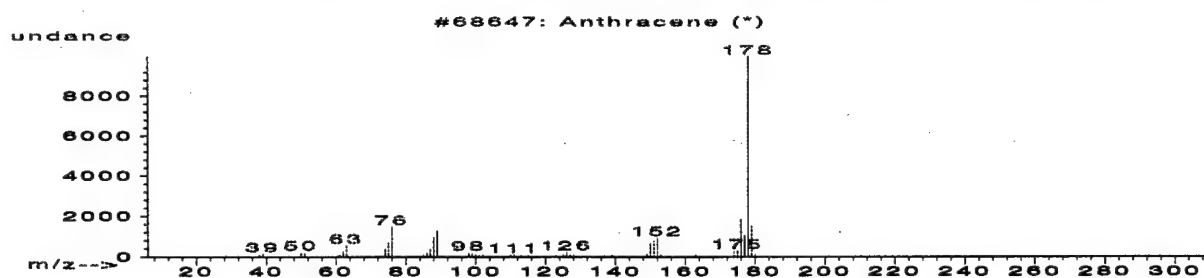
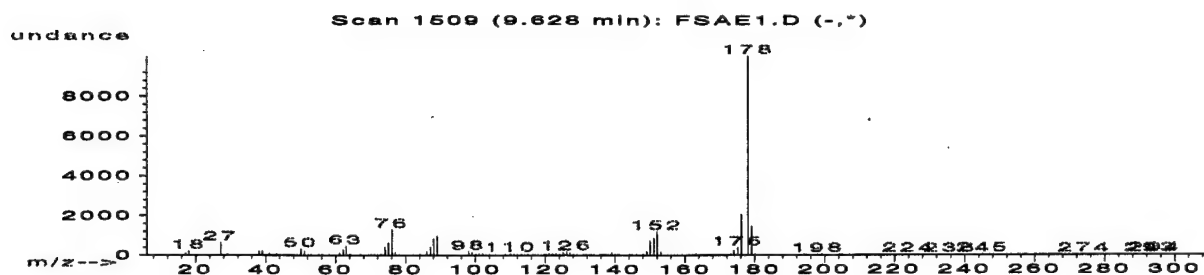
is no signal for mass 46 and essentially no signal for 30 (at least not in the area near 4 min where NO would elute), suggesting that sample B does not contain energetic materials or any other materials that yield a significant level of NO or NO₂. The mass spectra and library matches in Figure 4 indicate that the sample is composed primarily of hydrocarbons.

Since sample C is the residue collected from sample A after sample B had been removed, it follows that the extracted ion chromatograms from sample C should indicate the presence of pyrolysis products having masses 30 and 44 in that sample. Inspection of Figure 5 proves this to be true. The question that now remains to be answered is whether or not these products were generated by an energetic material or some other material. Examination of the other pyrolysis products generated by sample C can help answer this question. As indicated by the representative mass spectra (and library-search matches) given in Figure 6, most of the pyrolysis products of sample C are oxygen-containing hydrocarbons. Two of the major products look nearly identical to 4-hydroxy-4-methyl-2-pentanone and another matches well with 2,2'-oxybis ethanol. No fragments reminiscent of energetic material are observed (e.g., triazine from RDX or HMX). Based on the pyrolysis products observed, it is concluded that a major constituent of sample C is an oxygen-containing polymer that gives rise to formaldehyde (mass 30), and not NO, on pyrolysis.

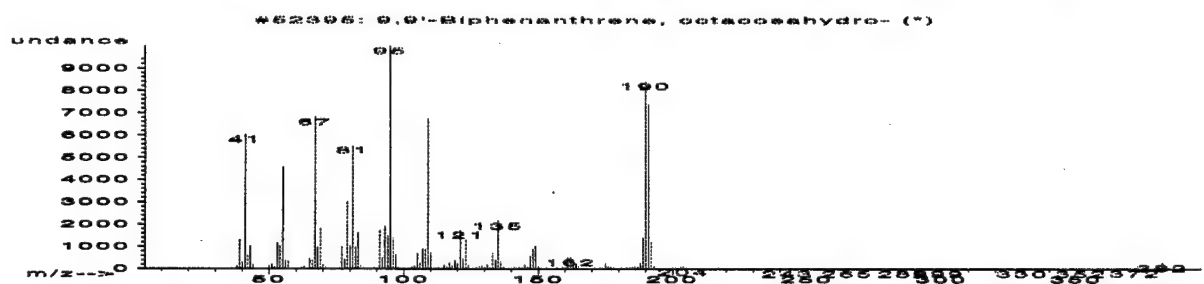
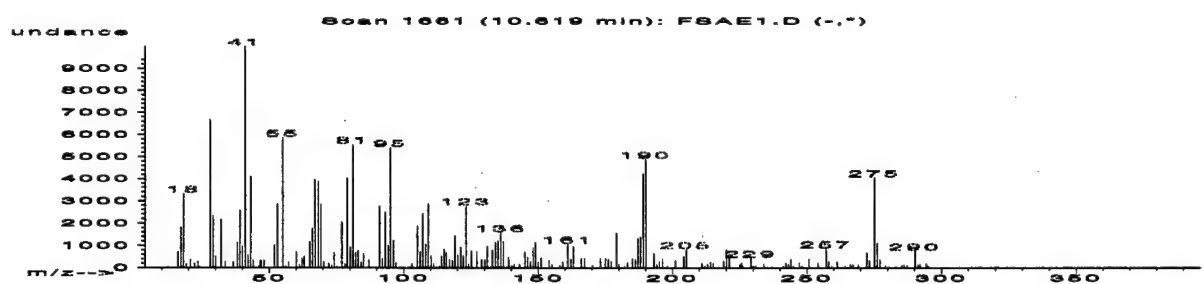
Further confirmation that sample C contains no energetic material was obtained by DSC analysis. As shown in Figure 7, when heated between the temperatures of 50 and 250° C, only a broad endotherm (indicative of a melting process) is observed. Had an energetic material been present, an exotherm would have likely been observed.

5. Conclusions

Based on the analyses reported here, it is concluded that the floor sweeping from Building 1107 contained no energetic materials.

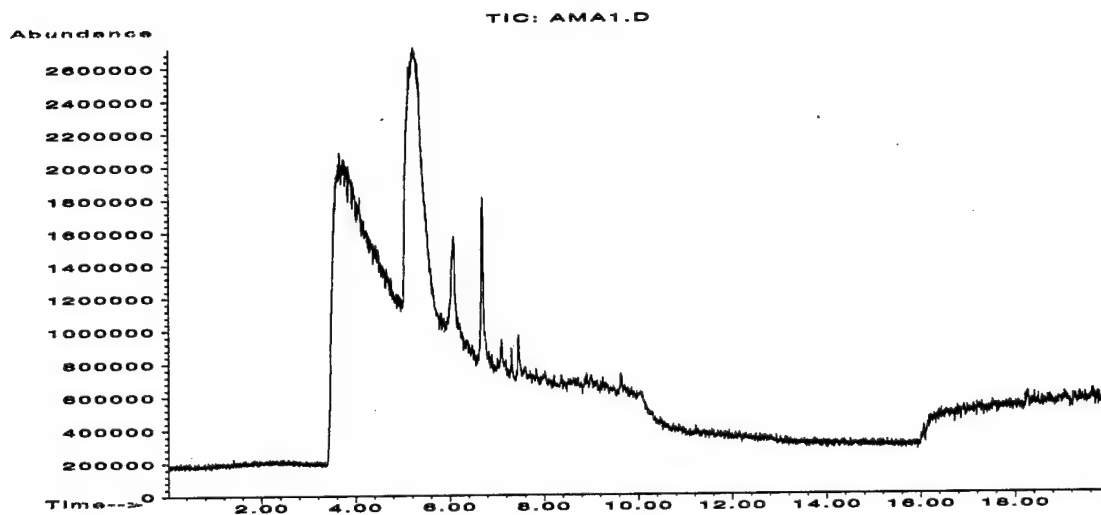


(a)

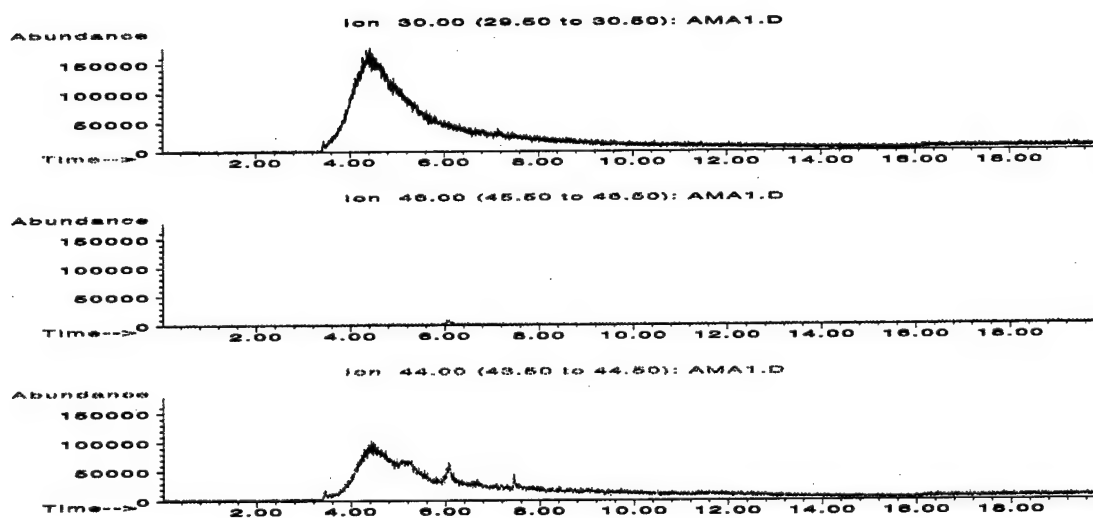


(b)

Figure 4. Mass Spectra and Library Search Matches for Two Peaks in Figure 2 (Sample B):
(a) 9.6-min Peak and (b) 10.6-min Peak.

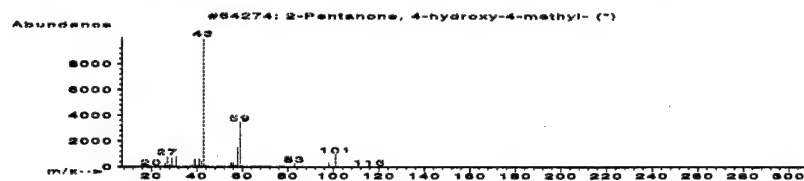
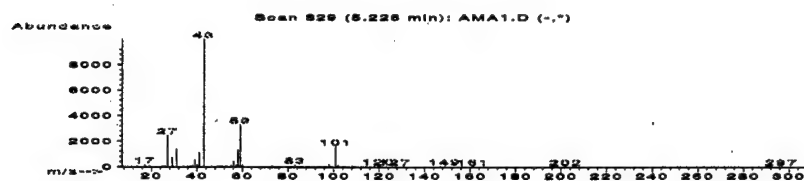


(a)

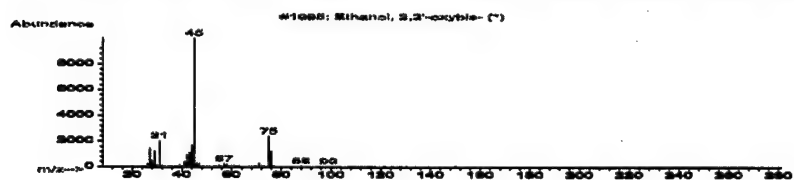
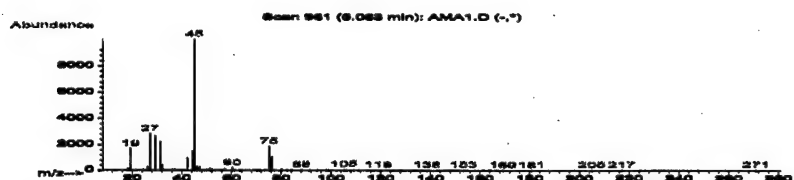


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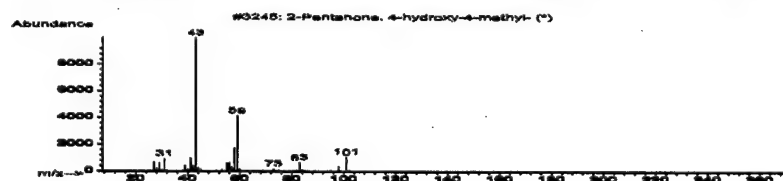
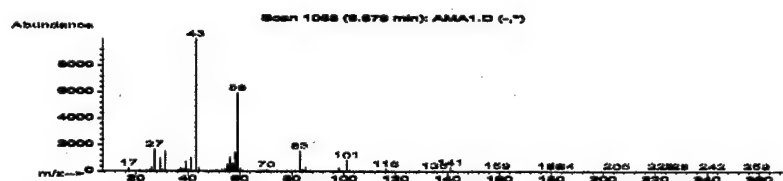
Figure 5. Gas Chromatograms for Sample C, Pulse Temperature = 175° C: (a) Total Ion Chromatogram and (b) Selected Ion Chromatograms.



(a)



(b)



(c)

**Figure 6. Mass Spectra and Library Search Matches for Peaks in Figure 4 (Sample C):
(a) 5.2-min Peak, (b) 6.1-min Peak, and (c) 6.7-min Peak.**

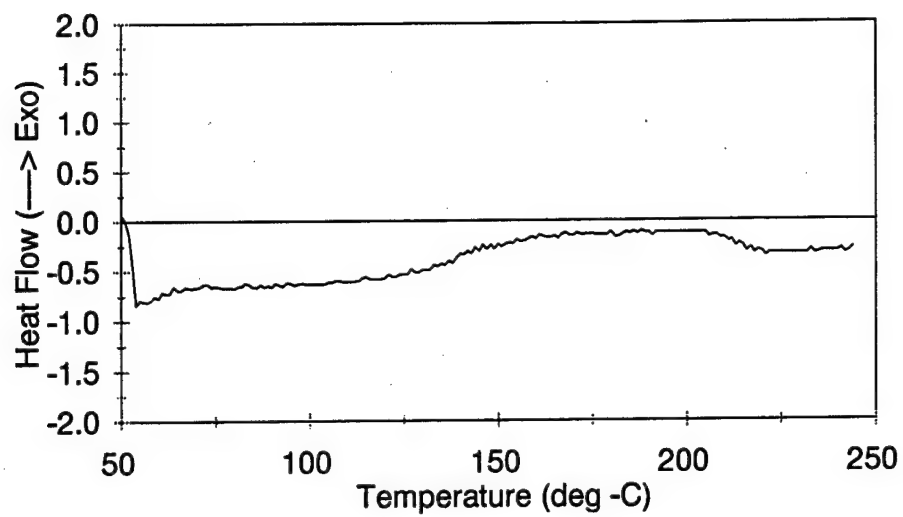


Figure 7. DSC Thermogram of Sample C.

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